Diffusion barriers in layered contact structures

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The concept of a diffusion barrier is discussed in the context of thin-film metallization systems. The conditions that an effective thin-film diffusion barrier should meet are enumerated. The dominant role of defects in determining the kinetic properties of a barrier layer is pointed out, and the consequent importance of the method of deposition and the parameters prevailing during deposition are stressed. Examples of the practically important cases of the stuffed barrier, the passive compound barrier, and the sacrificial barrier are given, with special emphasis on the latter as applied to Al contacting of silicide layers. Unconventional ways of forming multiple or novel diffusion barriers are briefly mentioned as well.

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I. INTRODUCTION

This review considers the role that thin-film diffusion barriers play in metallization schemes that are used for electrical contacts to a semiconductor, and to silicon in particular. Attention focuses on the processes that control the stability or instability of adjacent layers of conducting thin films along a direction perpendicular to the films. In VLSI structures, contacts are also laterally confined. This lateral confinement introduces additional constraints that can complicate the situation. These problems are not considered here.

In the past, progress in thin-film diffusion barriers has been based largely on empirical knowledge. The reason is that the information on the properties of materials necessary for a systematic approach to the problem is difficult to obtain. An adequate understanding sometimes requires materials characterization down to a near-atomic level, which calls for a combined use of advanced analytical tools. In recent years, the application of AES, SIMS, BS, TEM, and STEM to materials characterization has provided new capabilities in characterizing materials and thin films, and contributed considerably in resolving diffusion barrier problems. Section V gives an example that demonstrates our ability now to design contacts whose performance is predictable.

II. CONCEPT OF DIFFUSION BARRIERS

The need for a diffusion barrier arises when a material A is deposited on a substrate B and the two materials can intermix [Fig. 1(a)]. That process is accelerated during heat treatment in subsequent device processing or in operation. A well-known example is that of an Al film on a Si substrate. Both materials are uniquely suited for their respective functions in a semiconductor device, but they are unstable in contact with each other.

Aluminum has a finite solubility for Si at the device processing temperatures encountered after the Al deposition. This dissolution process can have destructive consequences. The idea of a diffusion barrier is to interpose a material X between A and B and thereby separate A and B from direct contact with each other [Fig. 1(b)]. The notion is derived from everyday experience where this remedy is employed frequently and successfully (painting wood, coating sheet metal). Ideally, the barrier layer X should meet three types of conditions:

(i) The transport rate of A and B across X should be small. In other words, the layer X should constitute a kinetic barrier to the traffic of A and B across it.

(ii) The barrier layer X should be thermodynamically stable against A and B, so that its existence in the presence of A and B is assured. In the minimum, a rate of loss of X into A and of X into B should be small.

(iii) The barrier layer X should adhere well to A and to B, have a low contact resistivity with A and B, have high electrical conductivity and thermal conductivity, be resistant to thermal and mechanical stress, and be laterally uniform in thickness and structure. These attributes make a barrier practically usable.

Note that a stable barrier is not necessarily a good kinetic barrier, because the transport of atoms across X can vary with factors such as pinhole density or defect structure of X. Also, a stable barrier will not react with A or B, which typically means poor adhesion. It is evident that the requirements listed above cannot be fully met all at once. Compromises must be sought.

An argument in support of the idea of diffusion barriers in thin-film form goes as follows. The diffusion constants for many atomic species in solid elements have been measured at high temperatures, where diffusion proceeds sufficiently rapidly to be readily measured. By determining the activation energy of the process, the diffusion constants at low temperatures can be extrapolated and the performance of thin-film barriers for a pair of elements can be computed. For instance, the diffusion constant of Cu in Ni is 3×10^{-12} cm^2 s^{-1} at 900°C[1] and has an activation energy of 61 kcal/mol.[2] At 300°C, $D_{\text{Cu in Ni}}$ is thus 3.8×10^{-24} cm^{2}s^{-1}, so that the time required for Cu to diffuse across a film of thickness $d = 1000$ Å is on the order $d^2/D \simeq 840\,000$ years. Nickel films have indeed been proposed as diffusion barriers for Cu in a solar cell metallization system,[3] yet experiments with pure, vacuum-deposited Cu/Ni bilayers have shown that the two metals begin to intermix at 350°C after 15 min of annealing in vacuum.[4]

The flaw in the preceding argument is the extrapolation

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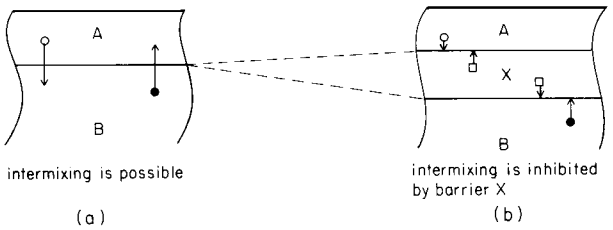

FIG. 1. A film of a metallic conductor (e.g., Al) on a substrate (e.g., Si) forms an unstable structure when A and B can intermix (a). The diffusion barrier X is interposed in an attempt to reduce this intermixing, but the number of possible degradation processes is increased.

of high-temperature data of diffusion constants to low temperatures. It has been known for a long time that below a temperature (known as the Tammann temperature) that is one-half to two-thirds the melting point of a solid (in K), atomic diffusion is no longer determined by regular bulk processes, but is controlled by the defects in the material. In thin films, where extensive defects such as grain boundaries or stacking faults sometimes reach across the whole thickness of the film, atomic diffusion processes via defects entirely dominate the kinetics in the film.[5,6] Arguments based on bulk properties then become irrelevant. The Tammann temperature for Cu is in the range of 400° to 600°C. The extrapolation of the high-temperature bulk diffusivity for Ni to 300°C ignores the major role of defects at low temperatures and yields completely erroneous predictions.

The inclusion of a barrier layer X always complicates the metallization scheme; but the simple presence of that additional layer does not necessarily improve the stability of the contact, as would be the case if the effectiveness of the barrier rested on its bulk characteristics. With thin films, the notion of a diffusion barrier can thus lead along a divergent path where the problems created by the added complexity increase faster than the improvements actually achieved. New contact schemes whose stability is attributed to diffusion barriers should always be viewed with sound suspicion.

III. ROLE OF DEFECTS IN THIN FILMS

The fact that defects determine the kinetic properties of thin films has immediate consequences. The number and the nature of the defects depend on the method used to deposit the film, and on the specific conditions prevailing during the deposition. It follows that the procedures applied in fabricating thin-film diffusion barriers are as important as the material used for the barrier. Success or failure can depend wholly on the method applied to produce the film. Diffusion barriers should be introduced in contacting schemes only after the beneficial effect of a barrier has been established over the whole range of production parameters encountered in practice.

Defects exist in a wide variety of forms. Among these, extended defects have particular significance for diffusion barriers. But the full characterization of defects is difficult. This explains why progress in this field has been largely empirical so far. The situation is likely to remain so, but the conceptual understanding of the basic processes controlling the low-temperature kinetics of thin films can offer very useful guidelines for experimental investigations, as the following example shows.

Gold is an attractive element for metallizations because of its high electrical conductivity, ease of evaporation, and inertness. Because of that low reactivity, Au adheres poorly to SiO_2. Titanium does react with SiO_2 and adheres very well to it.[7] A thin film of Ti is therefore frequently used as an initial layer of "glue" to assure adhesion. But Ti also reacts with Au if the two layers are brought into direct contact. One way to prevent this undesirable process has been to insert a layer of Mo between the Au and Ti films. This choice looks most favorable from the point of view of bulk properties: the solid solubility of Au in Mo is exceedingly small, and that of Mo in Au is less than 1 at.% below 600°C. However, the kinetic properties of a Mo film cannot be deduced from the bulk properties of Mo. From the point of view of a diffusion barrier, the kinetic characteristics are the relevant ones. Experiments have been performed that show that Mo films are permeable to both Au and Ti atoms when the layers are *e*-gun deposited under high vacuum conditions[8] [see Fig. 2(a)]. On the other hand, sputtered Mo layers are quite impermeable to Au when the sputtering conditions are chosen appropriately. The reason is attributed to impurities that are present in the sputtered layers and that alter the kinetic properties of the Mo film. Nowicki and Wang have convincingly demonstrated that the sputtering conditions alter the kinetic properties of a Mo film[9]: when the vacuum in the sputtering system prior to back-filling with Ar was better than 7.5×10^{-7} Torr, the films were permeable to Au [Fig. 2(a)]; if some N_2 gas was introduced into the sputtering system for a period of time during the Mo deposition, the layer became impermeable [Fig. 2(b)]. This experiment purposely exaggerated the amount of impurities usually present in a sputtering system, so that a change from the bcc equilibrium phase of Mo to a fcc structure was recorded as a result of the N incorporation. A recent study of a similar kind on $Ti_{0.3}W_{0.7}$ films established that the incorporation of about 7 at.% of oxygen substantially

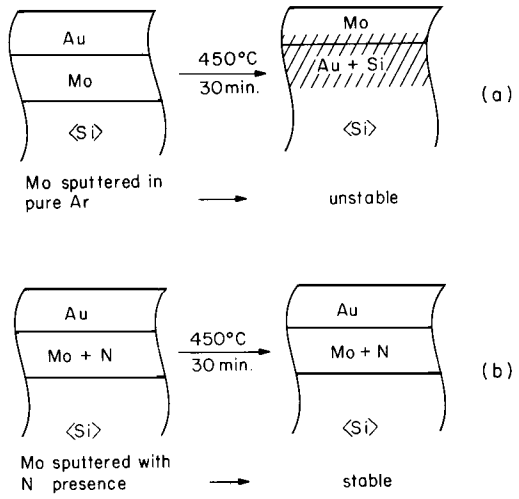

FIG. 2. The kinetic properties of a thin film depend on its method of fabrication. A Mo film, *e*-gun evaporated in high vacuum or sputter-deposited with Ar under clean conditions, is permeable to Au (a), but when N is added for a short period during a sputtering process, the barrier is tight (b).

improves the diffusion barrier properties of these films against Au penetration.[10]

The direct proof that defects determine the kinetic properties of thin films is obtained from a comparison of single-crystalline bilayers with their polycrystalline equivalent. Tu and Rosenberg found insignificant diffusion of Au through an epitaxially grown layer of Ag on a single-crystalline Au substrate after 48 h of vacuum annealing at 200°C, but a polycrystalline Ag layer did not prevent Au diffusion after only 24 h at 200°C.[11] The results were confirmed by Kirsch *et al.* in similar experiments.[12]

Unfortunately, single-crystalline layers are not a practical solution for diffusion barriers.

IV. PRACTICAL DIFFUSION BARRIERS

Diffusion barriers have been discussed and classified in a review paper that distinguishes three types of successful barriers.[13] The following examples are classified accordingly, but it should be noted that the classification of an example to a particular barrier type remains uncertain when the kinetic characteristics of the layers are unknown.

A. Stuffed barriers

The pronounced improvement of the diffusion barrier properties of Mo or $Ti_{0.3}W_{0.7}$ films in the presence of impurities such as O or N suggests that the rapid atomic diffusion at low temperature can be strongly suppressed by the segregation of impurities along the fast diffusion paths. Apparent volumetric concentrations of impurities ranging from 10^{-1} to 10^{-3} at.% are typical for grain boundary decoration. *Stuffed barriers* are those whose low atomic diffusivities are attributable to the inhibiting effect of impurities along fast diffusion paths. Impurity concentrations of 10^{-1} at.% or less are usually taken as indicative of this type of barrier (Fig. 3). To unambiguously establish this role of an impurity in a particular case is, of course, difficult, but there are many instances where the presence of stuffed barriers is likely. For example, two recent patents describe ways to effectively separate Al overlayers by depositing Cr,[14] or Al or Ta[15] films in a vacuum that is purposely contaminated with water vapor, air or oxygen; films deposited in a clean vacuum are ineffective barriers. Sputtered W layers have also been reported to effectively block interdiffusion between Al and an underlying silicide film.[16] Sputtering is a preferred deposition process for refractory transition metals; the process often introduces impurities. Stuffed diffusion barriers can be quite effective and are simple to make, but their use is treacherous when the essential role of a particular impurity is not recognized.

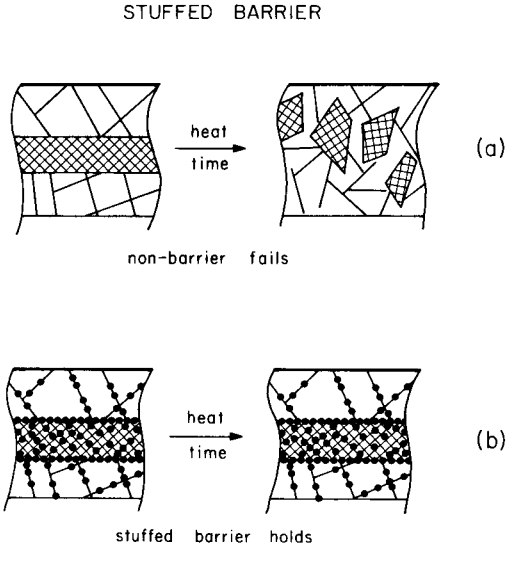

FIG. 3. A stuffed barrier owes its low atomic diffusivity to the presence of impurities along fast diffusion paths in the barrier material. Impurity concentrations of 10^{-1} at.% or less are an indication that such a condition may prevail.

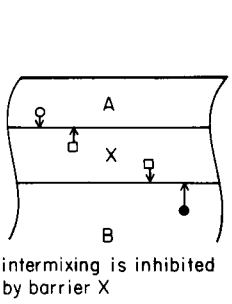

FIG. 4. A passive barrier is a film that has negligible diffusivities for A and B, that is chemically inert with respect to the materials A and B on either side of it, and that has negligible mutual solubility for and with A and B.

B. Passive compound barriers

The name *passive barrier* has been coined for the ideal film that is chemically inert with respect to the materials A and B on either side of it, that has negligible mutual solubility for and with A and B, and that has negligible diffusivities for A and B (Fig. 4). Since pure elemental layers of miscible and immiscible metals make poor diffusion barriers, compound materials constitute the remaining choice for barrier materials.

Compounds have the advantage of being numerous. By selecting strongly bonded materials, the chemical stability with respect to the materials on both sides of the barrier can be achieved. A good example of such a diffusion barrier is TiN, but nearly all nitrides, borides and carbides of early transition metals are attractive candidates for stable compound barriers.[17] These compounds are characterized by high electrical conductivity and a refractory nature (high melting points, chemical inertness, extreme hardness). Thin films are formed by sputtering of sintered compound targets or reactive sputtering of elemental target. Reactively sputtered TiN films have extremely fine grains on the order of a few hundred Angstrom in size.[18] The resistivity of the films increases rapidly with impurity content (such as oxygen) as a result of a decrease in the electron mobility,[18] but the diffusion barrier properties do not reveal a sensitivity to the oxygen impurity content.[19] Metallurgical tests show that reactively sputtered TiN films, a few kÅ thick on Si substrates with various overlain metal layers, change imperceptibly after thermal annealing in vacuum below the lowest metal–Si eutectic temperature.[20] After 11 h at 655°C, Cu and Ti interdiffuse at concentrations <10 at.% over only a ±300 Å zone centered on the TiN–Cu interface, indicating effective diffusivities on the order of

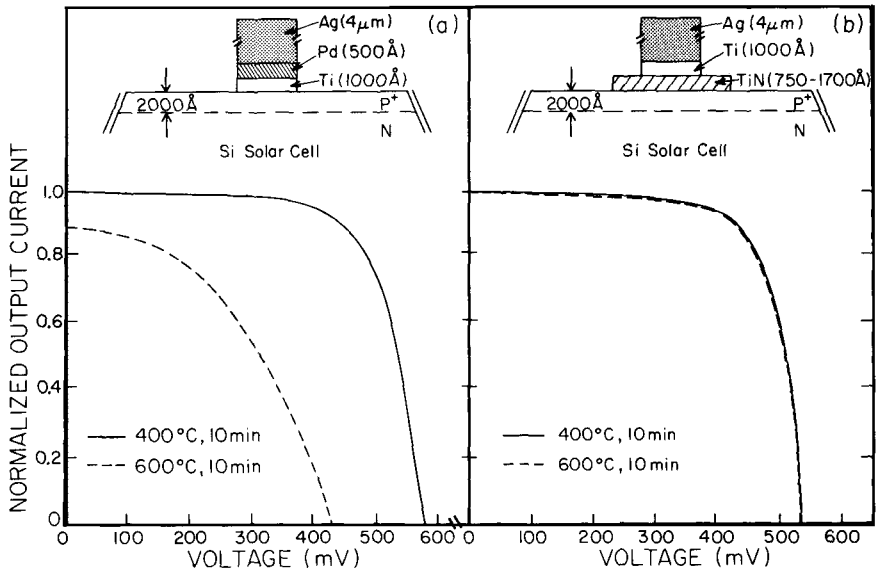

FIG. 5. I-V characteristic of a shallow-junction (~2 kÅ) Si solar cell under AMO illumination with the conventional Ti–Pd–Ag metallization system (a), and with a metallization scheme containing a reactively sputtered TiN diffusion barrier (b). The solid lines were measured after the usual 400°C, 10 min sintering treatment applied to the cells to minimize the contact resistance. The dashed lines were measured after thermal annealing at 600°C for 10 min in dry N_2.

10^{-17} cm^2/s with an activation energy of ~4 eV.[21] The diffusion process is unknown. Scaled to the melting of TiN (T_m ~ 2950°C), 655°C is only 0.29 T_m, which suggests that grain boundary diffusion should be dominant. It is indeed possible that reactively sputtered TiN films function as stuffed barriers, but overall, these layers behave as fair approximations of the ideal case of a passive barrier.

Figure 5 shows results of annealing tests of a silicon cell equipped with a reactively sputtered TiN diffusion barrier layer in its metallization scheme and of a cell with the conventional Ti/Pd/Ag metallization.[22] The effectiveness of the TiN barrier is quite evident. Measurements of the contact resistivity to n-type Si of TiN, HfN, TaN and related barrier layers have shown that values between 10^{-4} and 10^{-5} Ω cm^2 are typical.[23,24,25] Such values should produce insignificant power losses for solar cells approaching up to ×100 concentration. Contact resistivity values desired for high current-density circuits are on the order of 10^{-6} Ω cm^2.

Reactively sputtered TiN and TaN barriers have recently been successfully tested for a Ni metallization to PtSi layers on a Si substrate.[26] A 750 Å TiN barrier maintains the integrity of the contact after 90 min annealing at 600°C. Without the barrier, the Ni and PtSi layers would strongly intermix.[27]

C. Sacrificial barriers

Sacrificial barriers exploit the fact that thin adjacent films that react and form a compound often do so in a laterally very uniform fashion. A barrier layer X that reacts uniformly with the material A and B on either side of it then effectively maintains a separation of A and B as long as the barrier layer is not fully consumed by these reactions (Fig. 6). This point in time is predictable when the two reaction rates are known as a function of temperature, provided that precautions are taken to avoid interfacial impurities that might alter the reaction kinetics. Under those circumstances, the evolution of the barrier layer in time becomes predictable and a minimum barrier thickness can be quoted for any time-temperature cycle that the metallization scheme should survive. This degree of predictability is unique among diffusion barriers and confers to the sacrificial barrier a position of conceptual preeminence.

The first application of a sacrificial barrier that was recognized as such goes back to Bower who investigated the role of Ti as a diffusion barrier in the ⟨Si⟩/Ti/Al metallization system.[28] A recent patent describes the use of a sputtered film of the intermetallic compound $TaAl_3$ as a barrier between Al

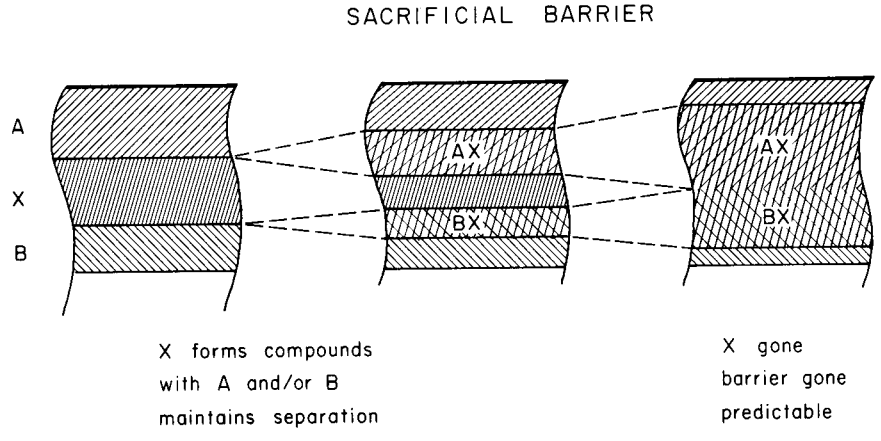

FIG. 6. A sacrificial barrier maintains the separation between A and B only for awhile, but that duration is predictable when the reactions with A and with B are laterally uniform and their rates are known.

and Ta on a Si substrate.[29] A Ta film does not react with a Si substrate below about 650°C, but a Ta film reacts with a superimposed Al film at about 450°C and forms a $TaAl_3$ interfacial layer.[30] The metallization system may thus be viewed as a sacrificial Ta layer whose consumption is anticipated by the sputter deposition of $TaAl_3$. Because that layer is sputtered, it may function in part as a stuffed barrier as well.

The next section describes the application of the sacrificial barrier concept to a practically relevant situation to exemplify this important method of contact design.

V. ALUMINUM CONTACTS TO SILICIDE LAYERS: AN EXAMPLE

Silicide films of Ni, Pd, and Pt can be formed uniformly and reproducibly at relatively low temperatures on Si substrates. These features are desirable to form shallow primary metallization layers for Si devices. Aluminum, on the other hand, is often the preferred choice for interconnections.

Experiments have established that the direct superposition of Al film on NiSi,[31] Pd_2Si,[32,33] PtSi,[34] $CoSi_2$, and $MoSi_2$[16] forms unstable systems. The cumulative evidence indicates that the metal silicide is transformed into a metal aluminide (identified as $NiAl_3$ for NiSi, and $PtAl_2$ for PtSi) beginning at the Al silicide interface and progressing as the square root of time. When the whole silicide layer is transformed and Al reaches the Si interface, the electrical properties of the contact change abruptly.

The system can be stabilized by using Ti, V or Cr as sacrificial barriers. The reaction of a layer of Pd_2Si on Si with a superposed Ti, V or Cr film has been investigated by several authors.[35–38] Detailed information available for Ti and Cr shows that Cr and Ti react with Pd_2Si on Si in essentially the same way they react with pure Si. For Cr, the reaction can take place at a slightly lowered temperature, and for Ti the reaction is slightly accelerated at the same temperature on Pd_2Si as compared to Si; but otherwise, the compound formed, the time, and the temperature dependence of the growth are unaltered and independent of the Pd_2Si thickness. As the silicide forms with Ti and Cr, the Pd_2Si layer moves further into the substrate. It is fairly safe to generalize these findings and say that films of the high-temperature silicide forming metals such as Ti, V, and Cr react with Si in the same fashion, whether deposited on Si substrates directly or on an interposed layer of NiSi, Pd_2Si or PtSi. The reaction of Ti, V, and Cr with those silicides is thus known for a given time and temperature cycle, and is laterally uniform. Table I summarizes the facts.

TABLE I. Parameters characterizing the reaction of thin films of Ti, V, and Cr on single-crystal silicon substrates.

Metal film on Si	Ti (Ref. 38)	V (Ref. 39)	Cr (Ref. 35)
Compound formed	$TiSi_2$	VSi_2	$CrSi_2$
Time dependence	$\sim t^{1/2}$ [a]	t ($t \lesssim 10$ min)	t
Temperature range (°C)	525–625	435–475	400–525
Activation energy (eV)	1.3	2.1	1.7
Growth rate	184 Å^2 s^{-1} @ 600°C[a]	1 Å s^{-1} @ 560°C	0.7 Å s^{-1} @ 450°C

[a] The $t^{1/2}$ time dependence was fitted to the $TiSi_2$ thickness observed at 600°C at 10 min; the actual reported time dependence is between $t^{1/2}$ and $t^{1/3}$.

TABLE II. Parameters characterizing the reaction of thin films of Ti, V, and Cr with an Al film. The last row gives the quantity of the metal film used as a sacrificial barrier that is consumed in the reaction.

Metal film under Al film	Ti (Ref. 28)	V (Ref. 40)	Cr (Ref. 41)
Compound formed	$TiAl_3$	VAl_3	$CrAl_7$
Time dependence	$t^{1/2}$	$t^{1/2}$	$t^{1/2}$
Temperature range (°C)	400–500	450–500	300–475
Activation energy (eV)	1.85	1.7	1.91
(Thickness of metal film consumed by compound)^2/ t (Å^{2}s^{-1})	$1.5 \times 10^{15} \times e^{-\frac{1.85\ \text{eV}}{kT}}$	$8.4 \times 10^{12} \times e^{-\frac{1.7\ \text{eV}}{kT}}$	$4.5 \times 10^{14} \times e^{-\frac{1.91\ \text{eV}}{kT}}$

The reaction of Al films with Ti, V, and Cr has also been well characterized. In all three cases, a compound is formed that grows parabolically with time and laterally uniformly at the Al–metal interface (see Table II).

The conditions of a laterally uniform reaction and of a known time-temperature behavior are thus fulfilled on both the silicide and the Al side of a sacrificial barrier for Ti, V or Cr. Values for the reaction rates are also available (Tables I and II). If now the requirement were to design a metallization scheme that would successfully pass an annealing test of, say, 15 min at 500°C, the answer derived from Tables I and II then is that a sacrificial barrier of Ti would have to exceed the value of 1.15 kÅ. The minimum thicknesses required for Ti, V, and Cr are given in Table III.

The validity of this solution can be compared for Cr against published data. From Olowolafe *et al.*,[42] it is found that with 500 Å of Cr between a bottom Pd_2Si layer on a Si substrate and a top Al film, about 250 Å of Cr was consumed by the silicide

TABLE III. Minimum thickness of a sacrificial barrier of Ti, V, or Cr needed to maintain the separation between a top Al layer and an underlying Si single-crystal, or a silicide layer of NiSi, Pd_2Si or PtSi on a Si single-crystal substrate, for thermal annealing at 500°C for 15 min.

Barrier metal film	Ti	V	Cr
Minimum barrier thickness x_m for 15 min @ 500°C (kÅ)	1.15	0.29	1.61
% of x_m reacted with Al	95	88	23.6
% of x_m reacted with Si	5	12	76.4
Holding time for the above barrier thickness at 300°C (days)	120	100	85

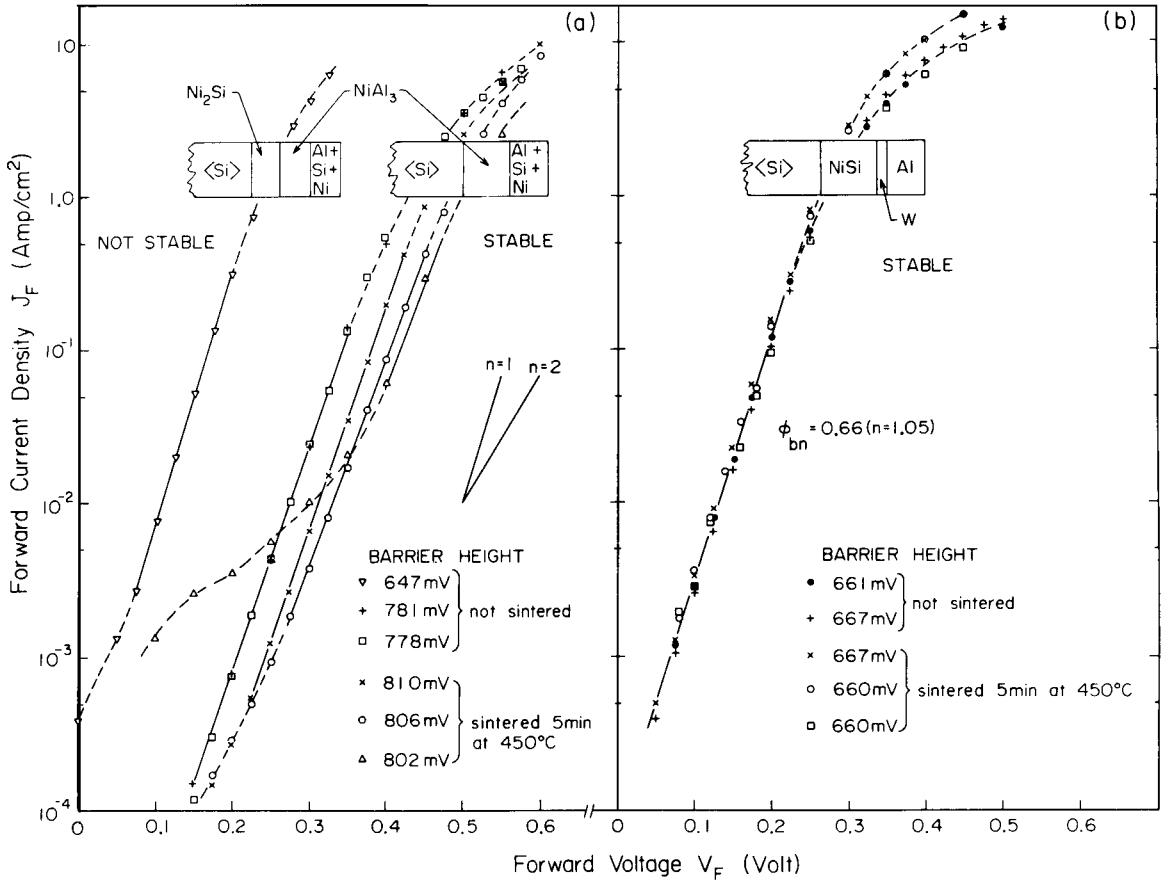

FIG. 7. $J(V)$ characteristics of NiSi Schottky barrier diodes before and after contact sintering for 5 min at 450°C with an Al metallization deposited directly on the Ni layer (a), and separated from the Ni by a vacuum-evaporated W barrier of 250 Å thickness (b).[43]

and Al compound formation after 10 min at 450°C. Tables I and II predict a minimum thickness of 260 Å for this heat treatment, an agreement we consider fortuitously close. For the case of Ti, the validity of the concept of a sacrificial barrier has also been tested electrically.[28]

Solutions to the same problem of separating Al from Ni, Pd, or Pt silicides can also be sought by using stuffed or passive diffusion barriers. Sometimes guidelines are available from experimental results published in the literature, or from experience, but no models of these barrier types exist at this time that would allow projecting from a paper design to reality, as can be done for the sacrificial barrier. For example, the solution suggested by van Gurp *et al.*[16] that employs a 2 kÅ sputtered W film as a diffusion barrier for $CoSi_2$, $Pt_xNi_{1-x}Si$ and $MoSi_2$ layers on Si has recently been investigated in detail for NiSi on Si.[43] It is found that vacuum-evaporated W films perform quite effectively as diffusion barriers below 450°C (see Fig. 7). Whether W acts as a passive barrier or a stuffed barrier is uncertain, nor is it known if the barrier would also work for Pd_2Si or PtSi. Experiments have shown that the W layer does not function as sacrificial barrier.

VI. FURTHER THOUGHTS

The specific diffusion barrier types listed in Sec. IV should not be considered the only ways to solve a practical contacting problem. Rather, these barrier types should be viewed as limiting cases between which practical cases will typically lie. From that vantage point, it is clear that there are many ways of conceiving a barrier, and that there is room for ingenuity and creativity in design. It is possible, for instance, to stack two (or more) diffusion barrier types in series. Examples are the systems ⟨Si⟩/PtSi/TiN/Ti/$TiAl_3$/Al and ⟨Si⟩/NiSi/TaN/Ta/$TaAl_3$(?)/Al recently investigated by Wittmer.[44] These systems combine a passive barrier (TiN or TaN) with a sacrificial barrier (Ti/Al or Ta/Al). In practice, the two layers of Ti (or Ta) and TiN (or TaN) can be deposited in a continuous sequence by timing the nitrogen flow during the film's reactive sputter deposition. The advantage of such combinations is that they offer additional flexibility in meeting conditions that a single barrier cannot. Passive barriers are inert and adhere poorly, but Ti is reactive and promotes adhesion. The fact that reactive transition metals are transformed into inert conducting materials by C, B or N can be most usefully exploited here.

Reducing the N content in a refractory metal nitride to small amounts converts a passive compound barrier (e.g., MoN) to a stuffed barrier. The example of Fig. 2 is of this type. The properties of a stuffed metal layer may differ much from those of a compound, and here again the choice can offer opportunities to optimize.

Another idea is to introduce impurities for the purpose of producing diffusion barriers by ion implantation. The process is attractive because of the accurate control it provides (yield) and because it is compatible with established technology. Stuffing a polycrystalline metal film that way would seem to be an obvious—as yet untested?—idea. A yet more daring

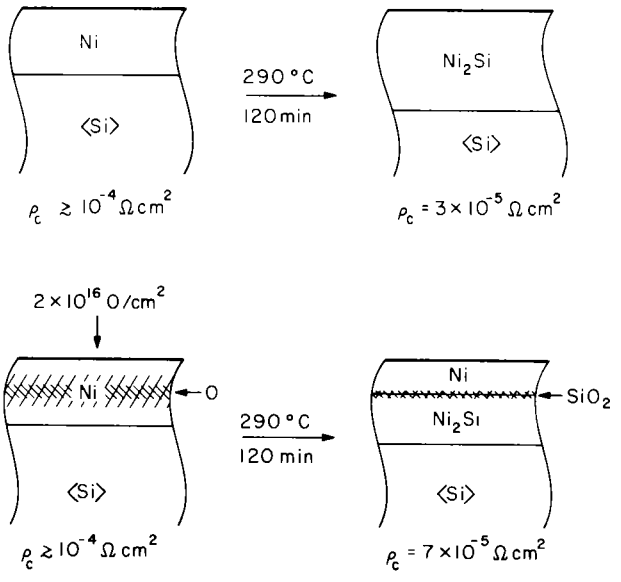

FIG. 8. Silicide-barrier-metal system formed by a single metallization and a single annealing step using ion implantation of an impurity (here oxygen) into the metal layer (here Ni) before thermal annealing to obtain a barrier.

thought is to construct the primary silicide layer of the contact, the diffusion barrier and the top metallization with a single metallization in a single annealing step (see Fig. 8). This concept has been successfully tested with a Ni film on a silicon substrate.[45] Prior to annealing, oxygen is implanted in the Ni film to a dose of about 10^{16} cm^{-2}. The oxygen forms SiO_2 when Si comes into contact with the implanted oxygen.[46] As the Ni–Si reaction proceeds, a layer of SiO_2 accumulates at the Ni_2Si–Ni interface. When the interfacial layer reaches an equivalent SiO_2 thickness of about 25 Å (for 1×10^{16} O/cm^2), the Ni consumption abruptly comes to a practical halt, thus forming a contact of the form Ni_2Si/(SiO_2-rich barrier)/Ni. The contact resistivity of $0.7\times10^{-4}\ \Omega cm^2$ of this system is only slightly higher than that of a pure Ni_2Si/Ni bilayer ($0.3\times10^{-4}\ \Omega cm^2$). A similar one-step metallization process can be carried out with other impurities[46–48] and metal films,[49] but the details depend strongly on the impurity–metal combination.

If extended defects present rapid diffusion paths, one way to eliminate them is to use amorphous conducting materials, also known as metallic glasses. These glasses can be produced from a large variety of different alloys, presenting a large scale of different properties.[50] One important parameter is the glass transition temperature T_g, which indicates a transition in kinetic parameters from values of a solid-like amorphous state to values of a liquid-like amorphous state. Refractory metals such as Nb, Hf or W in combination with a transition metal such as Fe or Ni, or a metalloid such as B or Si often form metallic glasses[51] with a T_g high enough to withstand the encapsulation process for semiconductor devices. Metallic glasses are generally more ductile than the corresponding polycrystalline compounds,[52] but the electrical resistivity is typically increased by a factor of 2–5.[53] Diffusivities are not yet well investigated but the available evidence shows that they are intermediate to those of defect-free single crystals and of polycrystalline materials.[54] Metallic glasses therefore seem to offer attractive possibilities as diffusion barriers. To our knowledge, no published information exists on that topic. Wiley *et al.*[55] have proposed metallic glasses as contact materials for semiconductor metallization. They also report on adhesion and recrystallization studies of such glasses (Nb–Ni, Mo–Ni, Mo–Si), and investigated the diffusivity of Au as did Chen *et al.* in Pd–Cu–Si.[54] Our own studies on the diffusion barrier properties of metallic glasses show that little intermixing occurs up to 30 min at 600°C for Fe–W–N layers between a Si substrate and Au or Cu metal films.

VII. CONCLUSION

Thermodynamically, a contact is unstable because it is not in a state of minimum free energy. To introduce a diffusion barrier is an attempt to slow down the equilibrating process. The instability itself is thereby not removed. Diffusion barriers thus cannot create true stability. The role of a diffusion barrier is merely to extend the lifetime of a contact to that of the projected use of the whole device. The incorporation of a diffusion barrier adds complexity and cost. It is basically an economic question how much the extension of lifetime is worth.

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